## THE IODINE CONTENT OF FRUITS AND VEGETABLES[1]

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### Abstract

The content of iodine in fruits and vegetables from the eastern Maritime Provinces has been determined by a modified Pfeiffer procedure. The sensitivity of the method was found to be about 1 μgm., with an accuracy of approximately ± 5%. The results obtained were near the mean values previously reported. The iodine content of potatoes varied from about 50 to 400 p.p.b. with a mean value of 153 p.p.b.; that of turnips from 50 to 90; several samples of cabbage, peas and pumpkin showed no trace of iodine present. Most specimens of fruit had no iodine, or only a trace, with the exception of plums which contained 113 p.p.b. No correlation of iodine content with variety or site of origin was evident.

Although numerous analyses of foods have been made for their content of iodine, very few have been carried out on foods of Canadian origin. This paper records analyses of iodine in the commoner fruits and vegetables from various districts of Nova Scotia and Prince Edward Island. These include several varieties of potatoes, turnips, carrots, parsnips, beets, squash, pumpkin, cabbage, cauliflower, corn, peas, beans, cucumber and tomatoes; apples, plums and pears.

### Experimental

*Material*

Seventy-eight samples of apples and pears from the Annapolis Valley, N.S., 16 samples of potatoes from various parts of Nova Scotia and Prince Edward Island, 25 samples of various fruits and vegetables from different districts of Prince Edward Island, and 19 samples of still other fruits and vegetables from Nova Scotia, have been collected. Not all were analyzed, because of the insignificant amounts of iodine found to be present.

These samples were washed, sliced, and then dried for a period of 24 hr. at 40° C. They were stored in glass jars. Prior to analysis they were dried at 100° C. to constant weight and ground in a Wiley mill to pass a screen of No. 20 mesh. All samples of potatoes were prepared with skin. Turnips, squash, and pumpkin were peeled but other vegetables were analyzed as a whole. Plums were stoned but apples and pears were sliced and dried in their entirety.

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## Method of Analysis

Many methods, differing in sensitivity depending on the amount of iodine present, have been developed for the estimation of iodine in biological material. Such methods require preliminary oxidation of organic matter, and no procedure has been generally accepted for this operation. Both dry and wet combustions have been used. Fusion with potassium hydroxide is very difficult with powders high in carbohydrate because of frothing and carbonization.

An attempt was made initially to follow the method of Kahane and Tomesco (3), who made use of a mixture of perchloric, nitric, and sulphuric acids for the digestion. The oxidation was not readily controlled and a violent explosion of unknown cause necessitated a modification of the procedure (6).

Oxidation, omitting the perchloric acid, was next attempted with a mixture of 3 ml. of concentrated nitric acid and 47 ml. of concentrated sulphuric acid to 1 gm. of dried sample. While this method gave correct results with recrystallized iodoform (99.2% recovery of iodine), with desiccated potato it required prolonged, careful heating. An attempt was made to carry out the digestion in an open vessel, as used by Chaney (1), but agreement in duplicate determinations was not satisfactory.

Digestion with concentrated sulphuric acid and 30% hydrogen peroxide by the method of Pfeiffer (4) was then tried. This procedure proved satisfactory as the initial stage. The estimation was completed by the method of Trevorrow and Fashena (5) and that suggested by Harvey (2), with certain modifications as described below. Replicate analyses were obtained at levels of iodine content of 100 p.p.b. or higher, with a precision of $\pm 2\%$. This decreased to about $\pm 5\%$ at lower levels of concentration. Recovery of known amounts of potassium iodide added to samples of potato was achieved with an accuracy of about 5%.

## Reagents

*Water* and *ethanol* (95%) were distilled after the addition of a small amount of potassium carbonate in an all-glass still.

*Potassium carbonate* was made into a paste with distilled water and extracted with redistilled ethanol (95%). The residue was dried and made into a saturated solution in redistilled water.

Other reagents were found to be free of iodine.
*Sulphuric acid*, 20% v/v, 50% and concentrated, analytical grade.
*Hydrogen peroxide*, 30% analytical grade.
*Bromine water*, analytical grade in redistilled water.
*Sodium thiosulphate*, 0.1 $N$ diluted each day to 0.001 $N$.
*Potassium iodide*, solid, analytical grade free of iodate.
*Starch*, 1%.

## Principle

Organic matter is oxidized in the presence of concentrated sulphuric acid and relatively large amounts of hydrogen peroxide. In this procedure any iodine present is liberated as such. This is driven off by a combination of air and steam, to be trapped as potassium iodide and hypoiodite. The latter substances are oxidized to iodate by hot aqueous bromine and titrated as iodine, in the presence of acid and excess of potassium iodide, with standard thiosulphate.
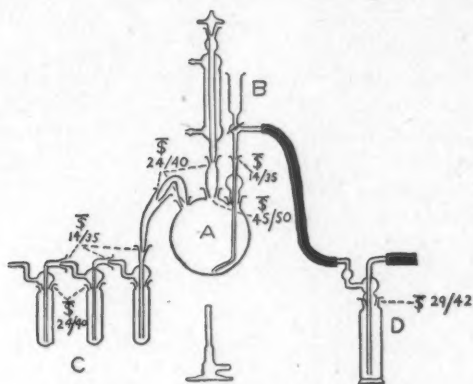


FIG 1.    *Apparatus for oxidation of organic material and absorption of iodine liberated.*

## Procedure

The apparatus was assembled for the most part of standard taper Pyrex glass parts as shown in Fig. 1. It consisted of a three-necked digestion flask (*A*) of 2 liters capacity. A reflux condenser, operated without water, was connected with the central neck and a glass stopper, standard taper 24/40, was inserted at the top of the condenser as shown. The gas-absorption tubes (*C*) were of 100 ml. capacity (obtained from the Scientific Glass Apparatus Co., Bloomfield, N.J., as parts of the distilling apparatus listed as J-1350). To each were added 10 ml. of a saturated solution of potassium carbonate and 40 ml. of redistilled water. A specially blown inlet tube (*B*) served for control of both liquid and air through a three-way stopcock. *D* is a gas-absorption bottle of 125 ml. capacity containing 50 ml. of aqueous sodium hydroxide (10%).

Twenty grams of dried sample was introduced into the digestion flask together with 200 ml. of 50% sulphuric acid. They were thoroughly mixed and the apparatus was connected as shown. Concentrated sulphuric acid (250 ml.) was added through inlet *B*. Compressed air was then slowly passed through the apparatus at a rate to ensure adequate mixing of the contents. Heat was applied at this point to the digestion flask, the amount of heat depending on the spontaniety of the reaction. Some samples did not require

any external application of heat until a large portion of the hydrogen peroxide had been added. This served to avoid excess foaming. Only a small flame from a Bunsen burner was used in the early stages of oxidation. Hydrogen peroxide (30%) was added slowly through $B$ in small portions to an amount of about 75 ml., the actual amount being governed by the rate of the oxidation. When the rate of reaction was decreasing, heat was applied to the flask, and the remainder of the hydrogen peroxide, usually about 25 ml., was added slowly while the mixture was fuming. When the sample was oxidized completely, as indicated by loss of color in the digestion mixture, the absorption bulbs were disconnected. The contents were washed into an evaporating dish and taken to dryness on a water bath. The residue was extracted with ethanol and the extract evaporated to dryness. The residue was dissolved in water, 3 to 4 ml. of freshly prepared bromine water added, and the whole acidified with sulphuric acid (20%). This mixture was boiled until free from bromine and then cooled. It was titrated with 0.001 $N$ sodium thiosulphate in a 1 ml. microburette, graduated in hundredths, after the addition of a few crystals of potassium iodide and 1 to 2 drops of starch (1%) as indicator. With the precautions outlined, a blank determination gave no color on the addition of the starch. The reaction is based on the equation
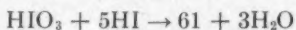
$$HIO_3 + 5HI \rightarrow 6I + 3H_2O$$
1 ml. $Na_2S_2O_3$ 0.001 $N \backsimeq$ 21.2 $\mu$gm. iodine (1/6 of 127).

The method has been found unsatisfactory by Trevorrow and Fashena (5) with fatty material. This difficulty has not entered into the present investigation because of the relatively insignificant amounts of lipid present.

*Results*

The analytical values obtained are recorded in Tables I and II. When the presence of iodine was detectable but so small as not to be measurable accurately, it has been recorded as a trace. On the basis of our technique this means less than 50 p.p.b. or 1 $\mu$gm. in 20 gm. of dried material. Results have been expressed in parts per billion on the basis of dry weight $\backsimeq$ $\mu$gm. per kgm. The presence of 50 p.p.b. or less in a food is indicative of a relatively poor source of iodine from a nutritional point of view.

Table I records the analyses on 16 samples of potatoes in four known varieties. The average content of iodine was 153 p.p.b., assuming a trace to represent approximately 25 p.p.b. No single variety was consistently higher than others and no locality was notably better in this respect, with the possible exception of Prince Edward Island. The average figure for iodine in potatoes as given in the literature is about 177 p.p.b., but excluding one very exceptional value of 1,045 it becomes 134.

TABLE I

ANALYSES OF POTATOES

| Source | Variety | Iodine content, p.p.b. |
|--------|---------|------------------------|
| Charlottetown, P.E.I. | Unknown | 153 |
| " | Irish Cobbler | 363 |
| " | " | 369 |
| Truro, N.S. | Unknown | < 50 |
| Hall's Harbour, N.S. | Irish Cobbler | < 50 |
| " | Katahdin | 114 |
| Kentville, N.S. | Irish Cobbler | < 50 |
| " | Green Mountain | 401 |
| " | Katahdin | 143 |
| " | Sebago | 105 |
| Scott's Bay, N.S. | Irish Cobbler | < 50 |
| " | Green Mountain | 66 |
| " | Katahdin | 114 |
| " | " | 109 |
| " | Sebago | 77 |
| Halifax, N.S. | Unknown | 334 |
| | Average | 153 |

TABLE II

ANALYSES OF VEGETABLES

| Vegetable | Source | Variety | Iodine content, p.p.b. |
|-----------|--------|---------|------------------------|
| Beans | Charlottetown, P.E.I. | Unknown | < 50 |
| | Alliston, P.E.I. | Webber Wax | — |
| Beets | Alliston, P.E.I. | Detroit Dark Red | 100 |
| | Kensington, P.E.I. | Unknown | — |
| | Charlottetown, P.E.I. | " | < 50 |
| Cabbage | Truro, N.S. | " | — |
| | Kentville, N.S. | " | — |
| | Charlottetown, P.E.I. | Golden Acre | — |
| Carrots | Alliston, P.E.I. | Hutchinson | 50 |
| | Charlottetown, P.E.I. | Chatenay | — |
| | Avonport, N.S. | Unknown | — |
| | Truro, N.S. | " | < 50 |
| | Kentville, N.S. | " | < 50 |
| Cauliflower | Charlottetown, P.E.I. | Snowball | — |
| Corn | " | Golden Bantam | < 50 |
| Cucumber | " | Snowball | < 50 |
| Parsnips | Kentville, N.S. | Unknown | < 50 |
| | " | " | — |
| Peas | Charlottetown, P.E.I. | " | — |
| | Kensington, P.E.I. | " | — |
| | Alliston, P.E.I. | " | — |
| Pumpkin | Charlottetown, P.E.I. | Small Sugar | — |
| Squash | " | Golden Hubbard | < 50 |
| Turnips | Kentville, N.S. | Unknown | < 50 |
| | Avonport, N.S. | " | 91 |
| | Truro, N.S. | " | 50 |
| | Charlottetown, P.E.I. | Laurentian | 81 |

Table II records all analyses carried out on vegetables other than potatoes. Turnips showed a measurable amount of iodine and most samples exhibited a trace. No iodine was detected in cabbage, cauliflower, peas, or pumpkin. With the exception of potatoes and turnips, vegetables in the eastern Maritime provinces are not notable for their content of iodine. Other investigators have found appreciable amounts in cabbage, carrots, and squash in North America.

Eleven samples of apples from 10 localities in Nova Scotia have been analyzed. The varieties included Baldwin, Blenheim, Cox Orange, Golden Russet, Gravenstein, Kings, McIntosh Red, Red Stark, Ribson, Wagener, and Wealthy. Of these the Gravenstein and Red varieties contained a trace of iodine while the rest were negative. One variety of pears and one of tomatoes contained no iodine, but plums, as the Bradshaw variety, exhibited a value of 113 p.p m. These results are in conformity with those of other investigators, with the exception of the results for tomatoes, which have been found to vary markedly in their iodine content.

## Discussion

It is apparent from the tables that fruits and vegetables from Nova Scotia and Prince Edward Island contain amounts of iodine comparable with median values as reported for other parts of the world. It is interesting to note that all samples that we have analyzed were harvested at a distance of less than 50 miles from the Atlantic ocean. This would suggest, a priori, a content of iodine above the general average, but this was not found to be true.

## Acknowledgments

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# THE OXIDATION, IGNITION, AND DETONATION
# OF FUEL VAPORS AND GASES

## IX. THE CAUSE OF THE REVERSAL OF THE ANTIKNOCK PROPERTY
## OF RICH HYDROCARBON-AIR MIXTURES[1]

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## Abstract

The experiments described show that conditions can be set in which a reversal of the antiknock effect of enriching a hydrocarbon–air mixture can be obtained in an unsupercharged engine. The reversal is of importance in respect of supercharged aero engines in which it may occur before mixture strength is increased to the value required for the development of maximum power. The experimental results, considered in the light of the nuclear theory of detonation, indicate that the "reversal" occurs when the rate of formation of finely divided carbon by pyrolysis of the fuel provides a proknock effect greater than can be offset by the antiknock effect of the products of the high temperature heterogeneous oxidation reaction.

## Introduction

The increase in usable compression ratio obtained on increasing mixture strength is due, aside from the cooling effect, to the corresponding increase in rate of surface oxidation of the fuel to antiknock products, Part VIII (3). Dilution of the end gas by the products lowers inflammability and offsets the tendency to nuclear ignition arising from impregnation of the end gas by finely divided carbon derived from pyrolysis of the hydrocarbon fuel, Part IV (2).

The increase of end gas temperature as compression ratio is raised and an increase in the concentration of hydrocarbon fuel in the mixture with air lead to an increase in rate of pyrolysis. It would be expected, therefore, that when using fuels prone to pyrolysis in high temperature conditions of engine operation the increased tendency to nuclear ignition might cease to be offset by the decrease in inflammability of the end gas arising from dilution with the products of high temperature surface oxidation. A *reversal* of the antiknock property of rich mixtures would then occur.

The object of the experiments described in this Part was to obtain the "reversal" in the conditions in which it would be expected to occur according to the theories mentioned.

## Experimental Arrangements and Selection
## of Hydrocarbon Fuel

The C.F.R. knock testing engine, unsupercharged, was used for the experiments in the manner described fully in Part VIII (3). The sole change was the provision of larger diameter fuel flow control orifices as required for increasing mixture strength beyond the degree used for the standard method of knock rating.

The high temperature operating conditions expected to be required were provided by the standard A.S.T.M. – C.F.R. motor method of knock rating, that is, the fuel–air mixture was heated to 300° F. and the jacket coolant maintained at 212° F.

Preliminary experiment demonstrated that a reversal of the antiknock property of rich mixtures of normal heptane, hexane, or pentane with air could not be obtained even in the relatively high temperature operating conditions. An indication of the effect was obtained, however, when the compression ratio at which heptane could be used was increased, on the addition of tetraethyl lead.

Fuel $S$ was then used for further experiments. It is a commercial gasoline of relatively high octane number as compared with $n$-pentane. The distillation graph, given by Fig. 1, Part VIII (3), shows an end point of 429° F. and that the fuel contains approximately 30% of constituents boiling above 300° F. The "heavy ends", probably long chain paraffins, would be especially prone to yield carbon on decomposition at the high temperatures of the end gas.

One set of experiments was made with fuel $S_1$, generally similar to fuel $S$ but of lower initial octane number raised to exceed that of fuel $S$ by being leaded. Unleaded fuel $S_1$ could not be obtained.

## Experimental Results

The experimental results are given by the graphs of Fig. 1, compression ratio for standard knock intensity, described as "usable compression ratio", being plotted against rate of fuel consumption, which represents mixture strength, engine speed being constant at 900 r.p.m. The minimum value of usable compression ratio for the undoped fuel $S$ was obtained when rate of fuel consumption was 1.85 lb. per hr. and it may be assumed that the mixture strength was then approximately correct. Maximum power, determined by later experiments, was obtained when rate of fuel consumption was 2.4 lb. per hr. The mixture was then nearly 30% "rich".

The reversal of the antiknock property of rich mixtures of fuel $S$ undoped, Graph (1), was obtained when the usable compression ratio attained the high value of 8.2, rate of fuel consumption being then 3.7 lb. per hr. and the mixture 100% rich. On adding tetraethyl lead to fuel $S$ in the concentration of 0.25 cc. per liter the "reversal" occurred at the higher usable compression ratio

of 9.3 but at the lower rate of fuel consumption of 3.4 lb. per hr., the mixture then being 84% rich. A similar "reversal" was obtained at a relatively low rate of fuel consumption when using fuel $S_1$, Graph (2). Comparable results for this fuel undoped are not given because a sample was unobtainable, as already mentioned.
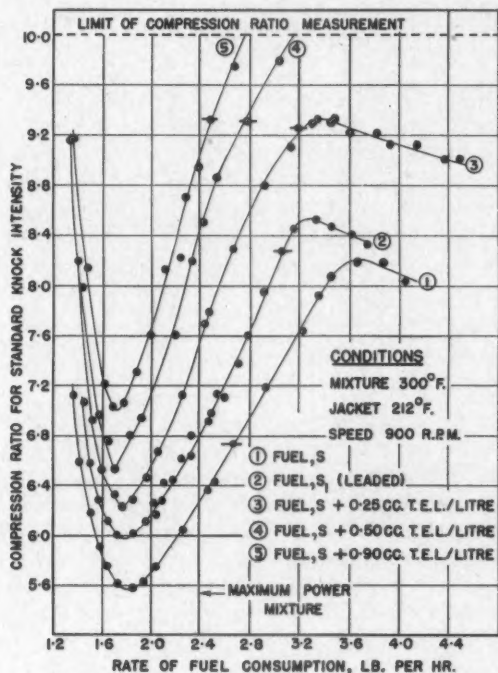


FIG. 1.   *Graphs showing the reversal of the antiknock effect of rich mixtures.*

When tetraethyl lead was added to fuel $S$ in the larger concentrations of 0.5 and 0.9 cc. per liter, usable compression ratio, Graphs 4 and 5, exceeded the 10:1 measurement limit before a "reversal" occurred.

The short horizontal lines on the graphs indicate the beginning of preignition which, however, never became sufficiently continuous to enable the engine to run with the spark ignition switched off.

Reversals of the antiknock property of rich mixtures were obtained when fuel $S$ contained iron or nickel carbonyl. The experimental results were so nearly like those, shown graphically by Fig. 1, for fuel $S$ leaded that they need not be described.

## Discussion

The rate of formation of antiknock products by high temperature hetero-geneous oxidation reactions in an engine is limited by the available area of active surface. On the other hand the rate of formation of proknock finely divided carbon by pyrolysis of the hydrocarbon fuel increases with the *quantity* inducted per stroke. The experiments described show that on increasing the quantity by using sufficiently rich mixtures a reversal of the antiknock effect of such mixtures was obtained in an unsupercharged engine, for the first time on record so far as known.

The reversal would be expected, according to the theory advanced, to occur in high duty supercharged engines when using leaner mixtures because the quantity of fuel inducted per stroke depends on supercharge pressure as well as on mixture strength. Thus if the combustible mixture be supplied at a pressure of say two atmospheres, the tendency to the formation of proknock carbon is doubled, other things being equal, while the rate of the hetero-geneous reaction producing antiknock compounds remains unchanged. The consequence is that in supercharged aero engines, which are commonly operated in high temperature conditions, a reversal of the antiknock effect of enriching the mixture may occur even before the attainment of the mixture strength required for maximum power.

The factors leading to the reversal seem to have first received attention in Germany, and developments have accordingly been described recently by Petty, Wright, and Garner (5, 6). Recent N.A.C.A. experimental work dealing with the subject has been described by Genco and Drell (1) and by Lord, Heinicke, and Stricker (4). The cause of the reversal effect is not discussed in the references mentioned.

## Acknowledgments

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